Structures of Si and Ge nanowires in the sub-nanometer range

R. Kagimura, R. W. Nunes, and H. Chacham

Departamento de Física, ICEX, Universidade Federal de Minas Gerais, CP 702, 30123-970,Belo Horizonte, MG, Brazil.
(Dated: February 2, 2008)

We report an *ab-initio* investigation of several possible Si and Ge pristine nanowires with diameters between 0.5 and 1.2 nm. We considered nanowires based on the diamond structure, high-density bulk structures, and fullerene-like structures. We find that the diamond structure nanowires are unstable for diameters smaller than 1 nm, and undergo considerable structural transformations towards amorphous-like wires. Such instability is consistent with a continuum model that predicts, for both Si and Ge, a stability crossover between diamond and high-density-structure nanowires for diameters smaller than 1 nm. For diameters between 0.8 nm and 1 nm, filled-fullerene wires are the most stable ones. For even smaller diameters (d $\sim$ 0.5 nm), we find that a simple hexagonal structure is particularly stable for both Si and Ge.

PACS numbers: 61.46.+w

Semiconductor nanowires with diameters of a few nanometers can be grown nowadays by vapor-liquid-solid [1, 2], solution-growth [3], or oxide-assisted growth methods [4]. These nanowires usually depict a crystalline core surrounded by an oxide outer layer. Further removal of the oxide layer by acid treatment may lead to hydrogen-passivated silicon nanowires as thin as one nanometer [4]. Pristine (non-passivated) silicon wires with diameters of a few nanometers have also been produced from Si vapor deposited on graphite [5]. The elongated shape of silicon and germanium clusters of up to a few tens of atoms, determined by mobility measurements [6, 7], indicates that even thinner pristine structures, with diameters smaller than 1 nm, can been produced.

The growth of such small-diameter structures raises the question of the limit of a bulk-like description of bonding in these nanowires, since for small enough diameters the predominance of surface atoms over inner (bulk-like) atoms will eventually lead to bonds (and structures) distinct from those of the bulk system. In the present work, we use first principles calculations to investigate several periodic structures of silicon and germanium pristine nanowires of infinite length, with diameters ranging from 0.45 to 1.25 nm. The nanowire structures considered are based on the diamond structure, fullerene-like structures, and the high-density bulk structures β-tin, simple cubic (sc), and simple hexagonal (sh).

Our calculations are performed in the framework of the density functional theory [8], within the generalized-gradient approximation (GGA) [9] for the exchange-correlation energy functional, and the soft norm-conserving pseudopotentials of Troullier-Martins [10] in the Kleinman-Bylander factorized form [11]. We use a method [12] in which the one electron wavefunctions are expressed as linear combinations of pseudo-atomic numerical orbitals of finite range. A double-zeta basis set is employed, with polarization orbitals included for all atoms. For the nanowire calculations, we employ super-cells that are periodic along the wire axis, and that are wide enough in the perpendicular directions to avoid interaction between periodic images. All the geometries were optimized until residual forces were less than 0.04 eV/Å. Total-energy differences were converged to within 4 meV/atom with respect to orbital range and k-point sampling.

Most of the nanowire structures we consider in this work are derived from crystalline structures. At zero pressure and temperature, the structure with the lowest energy per atom is the cubic diamond (cd), for both Si and Ge, and we use it as the reference structure in our calculations. As a first test of the methodology we employ, we compute the total energy per atom (E_{tot}), at zero pressure, for the following bulk phases: cd, hexagonal diamond (hd), β-tin, sh, sc, bcc, hcp, and fcc. In table I, we show the total energy per atom of each structure, $\Delta E_{tot} = E_{tot} - E_{tot}^{cd}$, relative to the total energy of the cd phase, E_{tot}^{cd}. We observe that ΔE_{tot} is within 0.20-0.45 eV/atom for the sc, sh, and β-tin phases, for both Si and Ge. Our ΔE_{tot} results for the sc, sh, and β-tin phases of Si, and for the β-tin phase of Ge are in good agreement with recent GGA calculations [13, 14]. As a further test of the reliability of our calculations, we consider the structural transition from diamond to β-tin, that occurs for both Si and Ge under pressure. The experimentally measured transition pressure is 117 kBar for Si and 106 kBar for Ge [15]. By computing the enthalpy $H = E + pV$ from constant pressure calculations, we obtained theoretical values of 124 kBar and 103 kbar for Si and Ge, respectively, both in very good agreement with the experimental values. These results also agree with previous GGA calculations [14, 16, 17].

We now address the structure and energetics of several stable structures of Si and Ge nanowires with diameters between 0.45 and 1.25 nm. Three classes of structures are considered. The first one derives from the cubic diamond (cd) bulk phase, with the nanowire axis oriented along (100) or (110). The latter corresponds to the usual orientation of observed Si nanowires with diameters between

TABLE I: Calculated total energies per atom (ΔE_{tot}), in eV/atom, of selected Si and Ge bulk phases, relative to the cubic diamond phase.

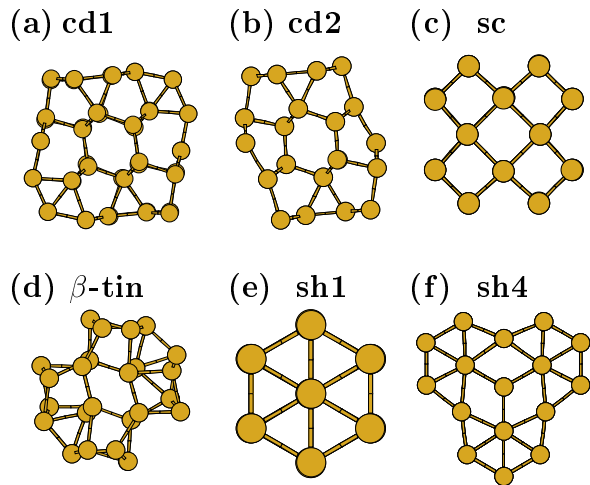|	hd	β-tin	sh	sc	bcc	hcp	fcc
Si	0.096	0.388	0.395	0.442	0.610	0.652	0.673
Ge	0.021	0.240	0.236	0.236	0.296	0.325	0.315

FIG. 1: Cross sections of selected Ge nanowire structures labeled according to the parent bulk phase. In (a) and (b), wires derived from the cubic diamond structure, with axis along (110) direction; in (c), a simple cubic wire; in (d), a $\beta - tin$ wire with axis along bulk c-direction; in (e) and (f), simple hexagonal wires with axis along bulk c-direction.
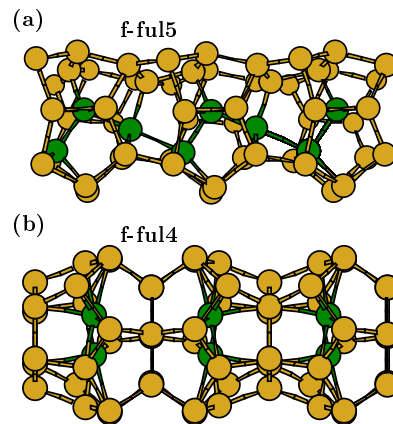

FIG. 2: Side view of corrugated Ge nanowire structures. In (a), corrugated wire resulting from a structural instability of a (100) cubic diamond nanowire; in (b), a filled-fullerene nanowire. Inner atoms are shown as green spheres.

3 and 10 nm [18]. The second class of structures derives from fullerene-like structures [5, 19, 20]. The third class of structures derives from the high-density β-tin, sc, and sh bulk phases. Our motivation for the study of the high-density structures initially came from the observation, in our *ab initio* calculations, of a structural instability of a (6,0) silicon nanotube which spontaneously deformed into a simple-cubic structure of considerably low formation energy, shown in Fig. 1(c). This finding led us to consider the β-tin and the sh high-density phases, which also have relatively small formation energies in bulk, as shown in table I. In the following, we describe the three classes of structures:

Diamond-structure nanowires - We considered several nanowires based on the cd structure with diameters between 0.5 nm and 1.2 nm, oriented either along (110) or (100). These structures were obtained from the cd bulk by defining the wire axis along the indicated crystalline direction, and by including atoms that fall within a specified distance from the axis. From this initial geometry, we removed low-coordinated surface atoms and performed geometry optimization using the *ab initio* scheme. For both Si and Ge, only the two widest wires, oriented along (110), remained diamond-like after geometry optimization. The geometries of these wires, labeled as cd1 and cd2, are shown in Figs. 1 (a) and (b) in the case of Ge. The corresponding structures for Si are very similar. Note that both the cd1 and cd2 wires undergo reconstruction at the surface but retain a crystalline core at the central interstitial channel. The diamond structure wires with diameters smaller than 1 nm suffered extensive reconstructions towards amorphous-like structures. Among these, we mention a wire oriented along (100), with a diameter of ~ 0.9 nm, which after reconstruction became corrugated with pentagonal rings at the surface. This wire is shown in Fig. 2 (a).

Fullerene-like nanowires - We considered two fullerene-based geometries proposed in Ref. [5], namely the Si_{20} cage polymer and the Si_{24} cage polymer. We label those structures as ful3 and ful4, respectively. Based on the predicted stability of filled-fullerene-like clusters [20], we also considered variations of ful3 and ful4, labeled as f-ful3 and f-ful4, with the inclusion of two extra atoms inside each cage. f-ful4 is shown in Fig. 2 (b). Its structure is corrugated and presents fivefold rings at the surface, resembling the wire shown in Fig. 2 (a). For this

reason, we classify the latter as fullerene-like, and label it as f-ful5. We further investigated filled fullerene-like nanowires of smaller diameter, which we label as f-ful1 and f-ful2. These are based on Si_{12} and Si_{16} cages, respectively, with one additional atom in the center of each cage.

High-density nanowires - The simple cubic (sc) Ge nanowire is shown in Fig. 1(c). It shows very little distortions relative to the bulk structure. The β-tin nanowire has its axis parallel to the bulk c-axis, passing through the center of an interstitial channel. While the initial geometry of this wire is somewhat similar to that of the sc nanowire, the corresponding relaxed geometries shown in Fig. 1 (c) and (d) are very different, due to the substan-

tial relaxation of the former. All four simple hexagonal (sh) nanowire structures are oriented along the bulk c direction, and retain the crystalline order along the wire axis after geometry optimization, regardless of the wire radius. Two of the sh structures, sh1 and sh4, are shown in Fig. 1(e) and (f), respectively. We also considered an empty-hexagon variation of the sh1 structure in which the central atom of the hexagon was removed. We label this structure as eh. The relaxed Si nanowires are structurally similar to the Ge ones shown in Fig. 1.
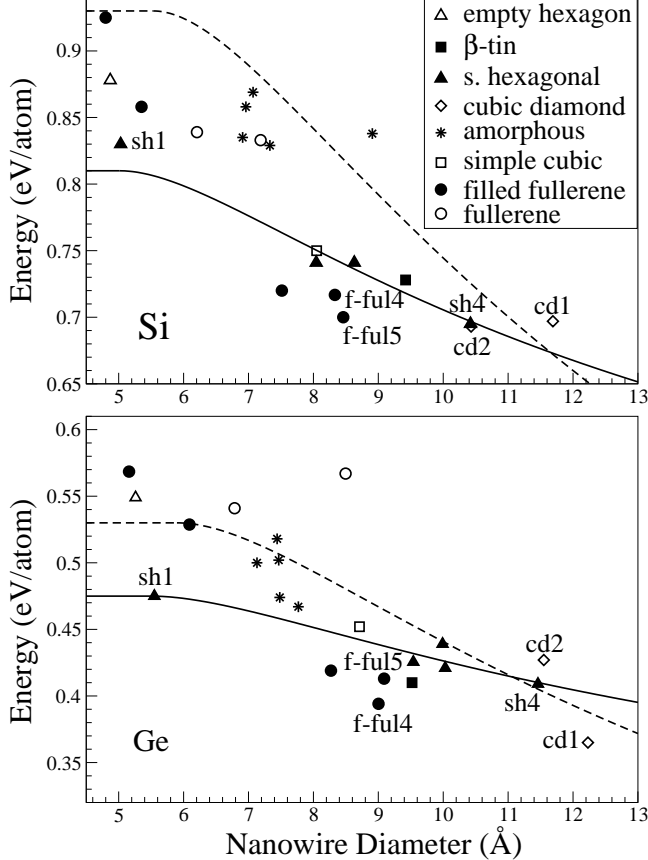

FIG. 3: Total energies per atom, ΔE_{tot} (in eV/atom, relative to cd bulk energy) of Si and Ge nanowires as a function of nanowire diameter. Labeled structures correspond to those shown in Figs. 1 and 2. explained in the text. Lines show the curves obtained from the continuum model (Eq. 1), with dashed (continuum) lines for nanowires based on the cd (sh) bulk phase.

The calculated total energies of the nanowires are shown in the Fig. 3, where we plot ΔE_{tot} as function of the nanowire diameter (defined as the diameter of the smallest cylinder that contains the nanowire). We observe that the formation energies of the high-density nanowires (based on sc, sh, and β-tin phases) and the fullerene-like nanowires, with diameters of the order of 1 nm, are very close to the energies of the diamond-structure nanowires cd1 and cd2, of similar diameters,

with energy differences of $\sim$0.05 eV/atom or less. Note that these values are one order of magnitude smaller than the energy differences of the corresponding bulk phases in Table I. This suggests that the energetics of wire formation in this diameter range is strongly affected by the surface atoms [21].

Figure 3 also shows that the amorphous wires derived from the instabilities of thin, diamond-structure wires, have higher formation energies than those of the high-density and the fullerene-like wires of similar diameter. This suggests that amorphous wires could only be produced in conditions very far from thermodynamical equilibrium. Cage structures like the unfilled fullerene structures and the empty-hexagon structures also have very high energies as compared to denser structures. The figure also shows that, among the nanowires of small diameters (smaller than 0.7 nm), the sh1 structure appears below and to the left in the energy vs. diameter diagram, which suggests a high stability for this structure, when compared to the other small-diameter geometries. In the diameter range between 0.7 and 0.9 nm, filled-fullerene-like wires are the most stable ones.

The above results suggest that the energetics of the formation of nanowires are determined by the interplay between the energy per atom of a "bulk" part of the wire and the corresponding energy of a "surface" part of the wire. Motivated by that, we elaborated a simple continuum model in terms of bulk and surface energies. Let us consider a cylindrical nanowire with radius R, number density ρ (number of atoms per volume), and total energy E_{nw}. By decomposing E_{nw} into a contribution due to the bulk-like atoms and a contribution due to the low coordinated surface atoms, we write $E_{nw} = \varepsilon_b \rho V_b + \varepsilon_s \rho V_s$ where ε_b is the total energy per atom of the bulk-like atoms, ε_s is the total energy per atom of the surface atoms, and V_b (V_s) is the volume occupied by the bulk-like (surface) atoms. V_b and V_s are determined by constraining the surface to a monoatomic layer, such that the surface thickness becomes $\rho^{-1/3}$. The total energy per atom, ε_{nw}, is then written as

$$\varepsilon_{nw} = \frac{E_{nw}}{N_{at}} = \varepsilon_s + (\varepsilon_b - \varepsilon_s)\frac{(R - \rho^{-1/3})^2}{R^2} \qquad (1)$$

for $R > \rho^{-1/3}$, where N_{at} is the number of atoms of the nanowire. For $R < \rho^{-1/3}$, $\varepsilon_{nw} = \varepsilon_s$.

To test our model, we apply Eq. 1 to nanowires based on the sh and cd bulk phases of Si and Ge. The parameters ε_b and ρ for the bulk phases are obtained from our *ab-initio* results for each bulk phase. The values of ε_s for the sh and cd phases are obtained from best fits to the first-principles calculations of the nanowires. In Table II, we show the fitted values of ε_s for the cd and sh phases of Si and Ge, as well as the difference $\Delta\varepsilon = \varepsilon_s - \varepsilon_b$ for each phase and material. The Table shows that $\Delta\varepsilon$ is about twice as large for the cd phase than for the sh phase for both Si and Ge. This means that the energy cost

TABLE II: Surface energy relative to the cd bulk energy ($\varepsilon_s - \varepsilon_b^{cd}$), in eV/atom, and relative surface energy within a given bulk phase ($\Delta\varepsilon = \varepsilon_s - \varepsilon_b$), in eV/atom, for sh and cd-based nanowires of Si and Ge.

	$(\varepsilon_s^{sh} - \varepsilon_b^{cd})$	$(\varepsilon_s^{cd} - \varepsilon_b^{cd})$	$(\varepsilon_s^{sh} - \varepsilon_b^{sh})$
Si	0.810	0.930	0.415
Ge	0.475	0.530	0.239

of a cd surface is much larger than that of a sh surface. This probably arises from the fact that surface atoms in a cd structure are undercoordinated (coordination three or less), while the surface atoms in a sh structure are still highly coordinated, which reduces the energy cost of the surface.

In Fig. 3 we plot ε_{nw} given by Eq. 1, relative to the total energy per atom of the cd bulk phase, as a function of the nanowire diameter for cd-based and sh-based nanowires of Si and Ge. The first-principles results for the sh phase fall very near ε_{nw}, which is a indication of the good quality of the model. We also notice that, although ε_s for the cd phase was fitted only to the cd1 and cd2 wires (the ones that retained the cd structure), the ε_{nw} curve also passes very near the calculated energies of the amorphous wires that originated from the cd structure.

The results of the continuum model seen in Fig. 3 clearly reproduce the trends of the first principles results. In particular, the model correctly describes the energy similarity of sh and cd nanowires for diameters around 1 nm. The model also predicts an inversion in the relative stability of sh-based and cd-based nanowires for a diameter D_c around 1.1 nm. This stability inversion results essentially from the larger ε_s for the cd phase as compared to the sh phase, for both Si and Ge. It is interesting to notice that the structural "transition" of the cd nanowires, from crystalline-like (for d > 1 nm) to amorphous-like (for d < 1 nm), occurs at diameters very near the stability inversion predicted by the model. This suggests that both effects are related, as the cd phase becomes "metastable" for d < 1 nm.

Finally, let us comment on the stability of the filled-fullerene-like structures and the sh1 structure for very small diameters. Although Eq. 1 cannot be applied to the filled-fullerene structures (there is not a bulk structure associated with them), their calculated energies behave as a decreasing function of the diameter. Such a hypothetical curve would cross that of ε_{nw} for the sh phase for diameters near 0.7 nm, as one can see from Fig. 3. This is consistent with the special stability of structure sh1 for very small diameters, and it suggests that the sh phase might be the stable one for ultra-thin nanowires.

In summary, we performed first-principles calculations of infinite, periodic wires of Si and Ge with diameters between 0.45 and 1.25 nm. We found that the diamond structure nanowires are only stable for diameters larger than 1 nm; thinner diamond-like wires undergo considerable structural transformations towards amorphous-like wires. We propose a continuum model to explain the energetics of the nanowires, on the basis of the competition between bulk and surface energies. According to this model, parametrized from the first-principles calculations, high-density nanowires become more stable than the diamond structure wires for diameters smaller than 1 nm. This is consistent with the structural instabilities of the diamond-structure nanowires. For diameters between 0.8 nm and 1 nm, filled-fullerene wires are the most stable ones. For even smaller diameters (d $\sim$ 0.5 nm), we find that the simple hexagonal structure is particularly stable for both Si and Ge.

[1] A. M. Morales, and C. M. Lieber, Science **279**, 208 (1998).
[2] H. Z. Zhang et al, App. Phys. Lett. **73**, 3396 (1998).
[3] J. D. Holmes et al, Science **287** , 1471 (2000).
[4] D. D. D. Ma et al, Science **299** , 1874 (2003).
[5] Bjorn Marsen, and Klaus Sattler, Phys. Rev. B **60**, 11593(1999).
[6] M. F. Jarrold, and V. A. Constant, Phys. Rev. Lett. **67**, 2994 (1991).
[7] J. M. Hunter et al, Phys. Rev. Lett. **73**, 2063 (1994).
[8] P. Hohenberg, and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn, and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
[9] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[10] N. Troullier, and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).
[11] L. Kleinman, and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982); X. Gonze, R. Stumpf, and M. Scheffler, Phys. Rev. B **44**, 8503 (1991).
[12] P. Ordejón, E. Artacho, and J. M. Soler, Phys. Rev. B **53**, R10441 (1996); D. Sánchez-Portal et al, Int. J. of Quantum Chem. **65**, 453 (1997). This methodology is implemented in the SIESTA program.
[13] C. Cheng, Phys. Rev. B **67**, 134109 (2003).
[14] N. Moll et al, Phys. Rev. B **52**, 2550 (1995).
[15] A. Mujica et al, Rev. Mod. Phys. **75/3**, 863 (2003), and references therein.
[16] K. Gaál-Nagy, P. Pavone, and D. Strauch, Phys. Rev. B **69**, 134112 (2004).
[17] As reported in Refs. [14, 16], LDA calculations understimate the cd-to-β-tin transition pressure.
[18] Y. Wu et al, Nano Lett. **4**, 433 (2004).
[19] Uzi Landman et al, Phys. Rev. Lett. **85**, 1958 (2000).
[20] U. Röthlisberger, W. Andreoni, and M. Parrinello, Phys. Rev. Lett. **72**, 665 (1994).
[21] Y. Zhao and I. Yakobson, Phys. Rev. Lett. **91**, 035501 (2003).